



Excellent hydrocarbon tolerance of CeO₂-WO₃-SnO₂ oxide catalyst for the NH₃-SCR of NO_x

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ABSTRACT

The tolerance of NH₃-SCR catalysts towards hydrocarbon compounds (HCs) is very important for their practical application on diesel vehicles. In this study, the HC resistance of CeWSnO_x, V₂O₅-WO₃/TiO₂ and Cu-SSZ-13 catalysts was systematically investigated using propene, toluene and *n*-pentane as model HCs. Experimental results suggested that the fresh and hydrothermally aged CeWSnO_x showed much better HC tolerance than the Cu-SSZ-13 and V₂O₅-WO₃/TiO₂. This property mainly originated from the strong HC oxidation capacity of the CeWSnO_x due to Sn introduction, which significantly inhibited side reactions, including the HC ammonoxidation and the carbon deposition reactions. In contrast, an undesired HC ammonoxidation reaction occurred at medium temperatures over the Cu-SSZ-13 and at medium-high temperatures over V₂O₅-WO₃/TiO₂, especially in the presence of propene, accompanied by the emission of toxic HCN gas. The high HC tolerance of CeWSnO_x gives it promise for application on heavy-duty diesel after-treatment systems in the future, especially those with the SCR-on-DPF or cc-SCR configuration.

1. Introduction

Nitrogen oxides (NO_x) emitted from diesel vehicles can cause serious air pollution, and increasingly stringent emission standards of NO_x have been launched worldwide. Selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) is a leading technique for NO_x removal from diesel exhaust [1,2]. In a common heavy-duty diesel vehicle aftertreatment system, the NH₃-SCR converter is installed downstream of diesel oxidation catalyst (DOC) and diesel particle filter (DPF) units to avoid poisoning of the NH₃-SCR catalysts by gaseous pollutants and diesel soot particles [3]. For this DOC+DPF+SCR after-treatment configuration, copper-exchanged small-pore zeolite NH₃-SCR catalysts (mainly Cu-SSZ-13), which exhibit satisfactory NH₃-SCR activity and hydrothermal stability, have been commercialized for diesel NO_x emission control at the EU VI and China VI stages [4]. It should be noted that unburnt HCs are always detected in real exhaust, especially during the cold-start period when the temperature of the exhaust gas stream is not high enough to initiate the DOC unit, or even in the warm-up period

when the upstream DOC catalysts are deactivated [5–7]. Besides, NH₃-SCR coupled with a lean NO_x-trap catalyst (LNT-SCR) system exposes the SCR unit to high concentrations of HCs during LNT regeneration, [8–10] which also requires the SCR catalyst to possess high HC tolerance. Additionally, a new promising strategy involving coating the NH₃-SCR catalyst directly on the DPF units (SCR-on-DPF) has been proposed recently for NO_x removal in heavy-duty and non-road applications. As a result, the SCR catalyst would be exposed to high concentrations of HCs during DPF active regeneration events, where HCs are injected to increase the temperature and trigger soot oxidation [1,8,11,12]. Moreover, to achieve the goal of ultra-low NO_x emission in the future, another smaller NH₃-SCR converter is designed to be installed at a location closer to the engine to increase the catalytic activity by taking advantage of passive thermal management, and thus this close-coupled NH₃-SCR catalyst (cc-SCR) should also possess high HC resistance when the DOC component is absent in the upstream of cc-SCR due to the limited space for installation [13,14]. To sum up, HC tolerance is crucial for the practical use of NH₃-SCR catalysts on diesel vehicles.

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The effects of HCs on the NH₃-SCR performance of Cu- or Fe-exchanged zeolites and the strategies to improve the HC tolerance of catalysts have been discussed in detail in the past decades [15,16]. Some properties of Fe- or Cu- exchanged zeolites can influence their HC resistance, such as surface acidity, topology, zeolite pore size and so on. It was reported that Fe-zeolite catalysts such as Fe-MOR, Fe-ZSM-5 and Fe-BEA suffered from activity loss in the presence of propene, which was due to coke blockage of the channels via acid-catalyzed reactions [17]. Li et. al suggested that the Fe³⁺ active sites of Fe-ZSM-5 were blocked by propene residue, which inhibited the capacity for oxidation of NO to NO₂, thus resulting in the loss of NH₃-SCR activity [18]. Based on a previous study, [19] the Cu-SSZ-13 catalyst (pore diameter ~0.38 nm) exhibited higher resistance to deactivation by heavy HCs than Cu-beta (pore diameter ~0.70 nm), which can be explained by the presence of 8MR small pores, where the NH₃-SCR can proceed largely free from the inhibitory effect of heavy HCs such as *m*-xylene or dodecane [20]. Accordingly, Cu-SSZ-13 catalysts have been investigated as SCR catalysts in advanced aftertreatment systems such as SCR-on-DPF [21]. However, the presence of light HCs, especially propene, was found to have a negative effect on the deNO_x efficiency of Cu-SSZ-13 catalysts, mainly at 300–400 °C [12,20,22,23]. Nam et. al reported in their recent research [20] that NH₃ could react with HCs over the Cu-SSZ-13 catalyst to form nitrile compounds through an ammoxidation reaction, especially at medium temperatures. This side reaction not only consumes the reducing agent NH₃, but also may trigger the formation of life-threatening substances, especially HCN [24,25]. Although Li et. al successfully improved the propene poisoning resistance of Cu-SSZ-13 by synthesizing a meso-CuSSZ-13 @mesoporous aluminosilicate (meso-Cu-SSZ-13 @MAS) catalyst, propene poisoning still cannot be avoided with this material [26]. All these showed that developing other NH₃-SCR catalysts simultaneously possessing high deNO_x efficiency and HC tolerance is still urgent.

Recently we developed a Ce-W-Sn composite oxide catalyst (hereafter referred to as CeWSnO_x) that exhibited fairly high effectiveness for NO_x reduction and superior hydrothermal stability [27]. Even after extreme hydrothermal aging treatment at 1000 °C for 3 h, this catalyst still showed > 90% NO_x conversion at 300–550 °C. Consequently, the CeWSnO_x catalyst has great potential for application on SCR units with the SCR-on-DPF configuration, where the NH₃-SCR catalyst would be exposed to high-temperature hydrothermal conditions during active regeneration of the DPF. To further evaluate the possibility of practical application of this catalyst for diesel emission control, the effects of hydrocarbons on the NH₃-SCR activity of the CeWSnO_x catalyst were systematically investigated in this work. For comparison purposes, the commercially available NH₃-SCR catalysts Cu-SSZ-13 and V₂O₅-WO₃/TiO₂ were also examined under the same conditions. Propene, toluene and *n*-pentane were selected as representatives of alkenes, aromatics and alkanes, respectively, due to their high abundance in diesel exhaust gas streams or relative ease of introduction into the reactor in gaseous form [17].

2. Experiment

2.1. Catalyst preparation

The CeWSnO_x catalyst with Ce: W: Sn molar ratio of 1: 0.24: 2 and the CeWO_x catalyst with Ce: W molar ratio of 1: 0.24 were prepared by a coprecipitation method using ammonium hydroxide as the precipitant, and the preparation details as well as the fundamental characteristics of the catalyst can be found in our previous publication [27]. The Cu-SSZ-13 zeolite used in this study was synthesized by a one-pot method followed by extra post-treatment with HNO₃ [28]. According to the results of inductively coupled plasma atomic emission spectroscopy (ICP-AES, OPTIMA 2000DV), the obtained Cu-SSZ-13 had a Cu content of 3.9 wt%, with Si/Al and Cu/Al molar ratios of 5.3 and 0.3, respectively. The commercial 2.5 wt% V₂O₅-6 wt%WO₃/TiO₂ catalyst,

shortened to V₂O₅-WO₃/TiO₂ in this study, was prepared by the wet impregnation method on a rotary evaporator, and the preparation details can be found in [Supporting Information](#).

Typically, the fresh catalyst was treated in a standard NH₃-SCR atmosphere with 859 ppm propene at 350 °C for 12 h to prepare hydrocarbon-poisoned (HCP) catalysts, and the obtained catalysts were named CeWSnO_x-HCP, V₂O₅-WO₃/TiO₂-HCP and Cu-SSZ-13-HCP, respectively. To prepare hydrothermally aged (HA) catalysts, the fresh catalysts (1 g) were hydrothermally aged at 750 and 850 °C, respectively, for 16 h in a feed gas of 10 vol% H₂O balanced by air (1 L min⁻¹). The obtained catalysts were denoted as Cu-SSZ-13-750/850HA and CeWSnO_x-750/850HA, respectively, for simplicity.

2.2. Catalytic activity tests

The catalytic activity tests were carried out in a quartz tube plug flow reactor. The simulated reaction gases consisted of 530 ppm NH₃, 500 ppm NO, 5 vol% O₂, 5 vol% H₂O and balance N₂ (namely the standard NH₃-SCR atmosphere) with different kinds of hydrocarbons (0/430/859/2579/3439 ppm of propene, 0/41 ppm of toluene or 0/405 ppm of *n*-pentane) dosed optionally. The total flow rate equaled 500 mL/min unless otherwise specified. The effects of different gas hourly space velocities (GHSV, 60, 000–480, 000 h⁻¹) on the NH₃-SCR performance in the presence or absence of 859 ppm propene were also investigated by varying the amount of catalyst used. To avoid the impacts of gas adsorption, the steady-state activity data of different catalysts at each target temperature were recorded using the same dwell time protocol (Table S1). Propene-SCR experiments were carried out under the same conditions of NH₃-SCR without adding NH₃ into the feed gas mixture. Oxidation experiments of different components (propene+O₂, NH₃+O₂ or propene+NH₃+O₂) were also performed on the same device with the addition of target gases to the 5 vol% H₂O+ N₂ gas flow. The gas compositions were continually analyzed with an FTIR spectrometer (IS10 Nicolet), which was equipped with a multiple path gas cell (2 m).

The NO_x, NH₃ and HC conversion in different reactions were calculated as follows:

$$\text{NO}_x \text{ conversion} = \left(1 - \frac{[\text{NO}_x]_{\text{out}}}{[\text{NO}_x]_{\text{in}}}\right) \times 100\% \quad (1)$$

$$\text{NH}_3 \text{ conversion} = \frac{([\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}})}{[\text{NH}_3]_{\text{in}}} \times 100\% \quad (2)$$

$$\text{HC conversion} = \frac{([\text{HC}]_{\text{in}} - [\text{HC}]_{\text{out}})}{[\text{HC}]_{\text{in}}} \times 100\% \quad (3)$$

where [NO_x] = [NO] + [NO₂], and [NO_x]_{in/out}, [NH₃]_{in/out} and [HC]_{in/out} denote the inlet/outlet gas concentrations of NO_x, NH₃ and HC, respectively.

2.3. Catalyst characterization

Thermogravimetry-mass spectrometry (TG-MS) analysis was carried out on a TGA/DSC 1 STARE analyzer (Mettler-Toledo) coupled with an online GSD 350 ThermoStar Mass Spectrometer (Pfeiffer-Vacuum). The TGA furnace was heated from 50 to 850 °C with a heating rate of 30 °C/min in flowing air (50 mL/min).

In-situ diffuse reflectance infrared Fourier transform spectroscopy (in-situ DRIFTS, IS50 Nicolet) experiments were performed on a Thermo Nicolet IS50 spectrometer. Before adding reaction gases, the catalyst powder was first pretreated at 500 °C for 30 min in air (500 mL/min) and then cooled down to the target temperature (200–500 °C). The adsorption experiments of propene+O₂, NH₃+O₂ and propene+NH₃+O₂ were carried out by exposing the catalyst to the appropriate gas mixture for 30 min and then purging with N₂ for another 10 min. The simulated reaction gases consisted of 530 ppm NH₃ (when used),

859 ppm propene (when used), 5 vol% O₂ and balance N₂. IR spectra were recorded by averaging 100 scans with a resolution of 4 cm⁻¹.

3. Results

3.1. NH₃-SCR performance in the presence of different HCs

The steady-state NH₃-SCR activities of CeWSnO_x, V₂O₅-WO₃/TiO₂ and Cu-SSZ-13 catalysts in the absence and presence of different HCs (including propene, toluene and *n*-pentane) were evaluated at 150–550 °C, respectively. The effects of HCs on NO_x conversion (Fig. 1) and N₂O by-product formation (Fig. S1) were negligible for all the three catalysts at temperatures below 250 °C. In the medium-high temperature range above 250 °C, however, the presence of HCs influenced the NH₃-SCR performance of catalysts differently. Specifically, the CeWSnO_x catalyst showed much higher anti-HC performance than the V₂O₅-WO₃/TiO₂ and Cu-SSZ-13 catalysts, and more than 90% NO_x conversion was still maintained at 250–500 °C in the presence of propene, toluene or *n*-pentane (Fig. 1). Besides, the almost identical conversion rates of NO_x and NH₃ at 250–450 °C (Fig. S2) indicated that the standard NH₃-SCR reaction proceeded stoichiometrically over the CeWSnO_x catalyst in the presence of HCs, from which it was clear that side reactions relating to NH₃ consumption were not significant on this catalyst. Contrarily, all three HCs showed inhibiting effects on the NH₃-SCR activity of the V₂O₅-WO₃/TiO₂ catalyst at 250–550 °C in the order propene > *n*-pentane > toluene (Fig. 1). For the Cu-SSZ-13 catalysts, the NO_x conversion in the medium-temperature (~250–450 °C) region decreased upon propene addition (Fig. 1a), while remaining unchanged after introducing toluene or *n*-pentane (Figs. 1b–1c). It should be noted that the side effects of propene on the Cu-SSZ-13 catalyst were especially problematic since the related temperature range for the decrease of NO_x conversion overlapped with the inlet temperature (200–450 °C) of the SCR unit of the heavy-duty diesel vehicle [29]. Another novel finding was that the NH₃ conversion was greater than the NO conversion at 250–550 °C for the V₂O₅-WO₃/TiO₂ catalyst (Fig. S3) and at 250–450 °C for the Cu-SSZ-13 catalyst (Fig. S4) in the presence of propene, suggesting that undesirable consumption of NH₃ occurred on the V₂O₅-WO₃/TiO₂ and Cu-SSZ-13 catalysts via the direct oxidation of ammonia and/or propene ammoxidation [20,30]. The NH₃ conversion in the propene&NH₃&O₂ reaction tended to be higher than that in the NH₃&O₂ reaction over the V₂O₅-WO₃/TiO₂ and Cu-SSZ-13 catalysts (Fig. S5), further verifying that the presence of propene promoted the consumption of NH₃. Together, the results above confirmed that the CeWSnO_x catalyst showed the most outstanding hydrocarbon tolerance among the three catalysts.

3.2. Propene tolerance of hydrothermally aged catalysts

Both the hydrothermal stability and HC resistance are important for NH₃-SCR catalysts used in practical SCR-on-DPF units due to the injection of fuel during active regeneration of the DPF (Fig. 2a). According to the NH₃-SCR performance results (Fig. 1), the poisoning effects of propene on the NH₃-SCR performance of all the three catalysts are more serious than those of toluene and *n*-pentane. Accordingly, the effects of propene on the NH₃-SCR performance of CeWSnO_x and Cu-SSZ-13 catalysts that were hydrothermally aged at 750 °C and 850 °C for 16 h were further studied in this work. It should be pointed out that the V₂O₅-WO₃/TiO₂ catalyst was not involved in this section since it was deactivated severely after hydrothermal-aging treatment at 700 °C for 10 h [31]. As shown in Figs. 2b–2c, the NO_x conversion of CeWSnO_x-750HA and Cu-SSZ-13-750HA catalysts showed little difference compared with their fresh counterparts in the absence of propene, indicating that both catalysts showed excellent hydrothermal stability at 750 °C. With the inclusion of propene in the feed gas stream, the NO_x conversion of the CeWSnO_x-750HA catalyst only showed a slight decrease (Fig. 2b), while the Cu-SSZ-13-750HA catalyst underwent more detrimental deactivation, especially at 250–450 °C (Fig. 2c). Besides, although the side effects of propene on the NH₃-SCR performance of CeWSnO_x catalysts were slightly intensified with the increase of hydrothermal-aging temperatures from 750 to 850 °C, > 80% NO_x conversion was still realized at 250–500 °C on the CeWSnO_x-850HA catalyst in the presence of propene (Fig. 2b). The Cu-SSZ-13-850HA catalyst, however, completely lost its deNO_x efficiency in the absence or presence of propene (Fig. 2c). In summary, the hydrothermally aged CeWSnO_x catalyst showed higher anti-propene properties than the aged Cu-SSZ-13 catalyst.

3.3. Influence of propene concentration and GHSVs

The influence of propene concentrations up to 3439 ppm on the NH₃-SCR performance of the CeWSnO_x catalyst was evaluated. As shown in Fig. 3a, the NO_x conversion profile in the presence of 430 ppm propene showed little change compared with that in the absence of propene at all tested temperatures. At higher propene concentrations (859/2579/3439 ppm), the NO_x conversion slightly decreased at 250–450 °C and seriously decreased at 500–550 °C. Meanwhile, increasing the concentration of propene showed little negative effect on the propene conversion (Fig. 3b). This finding supported the viewpoint that the reaction relating to propene consumption was kinetically faster than the NH₃-SCR reaction over the CeWSnO_x catalyst.

The NH₃-SCR performance of the CeWSnO_x catalyst in the presence

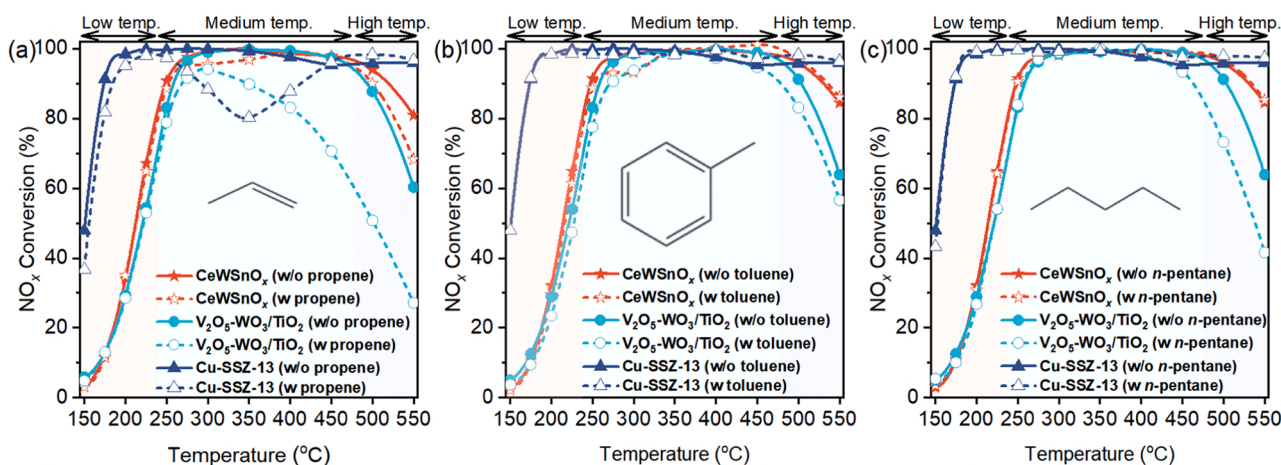


Fig. 1. NO_x conversion of CeWSnO_x, V₂O₅-WO₃/TiO₂ and Cu-SSZ-13 catalysts for the NH₃-SCR reaction without (w/o) and with (w) propene (a), toluene (b) and *n*-pentane (c). Reaction conditions: 530 ppm NH₃, 500 ppm NO, 859 ppm propene (when used), 41 ppm toluene (when used), 405 ppm *n*-pentane (when used), 5 vol% O₂, 5 vol% H₂O and balance N₂ with GHSV = 120, 000 h⁻¹.

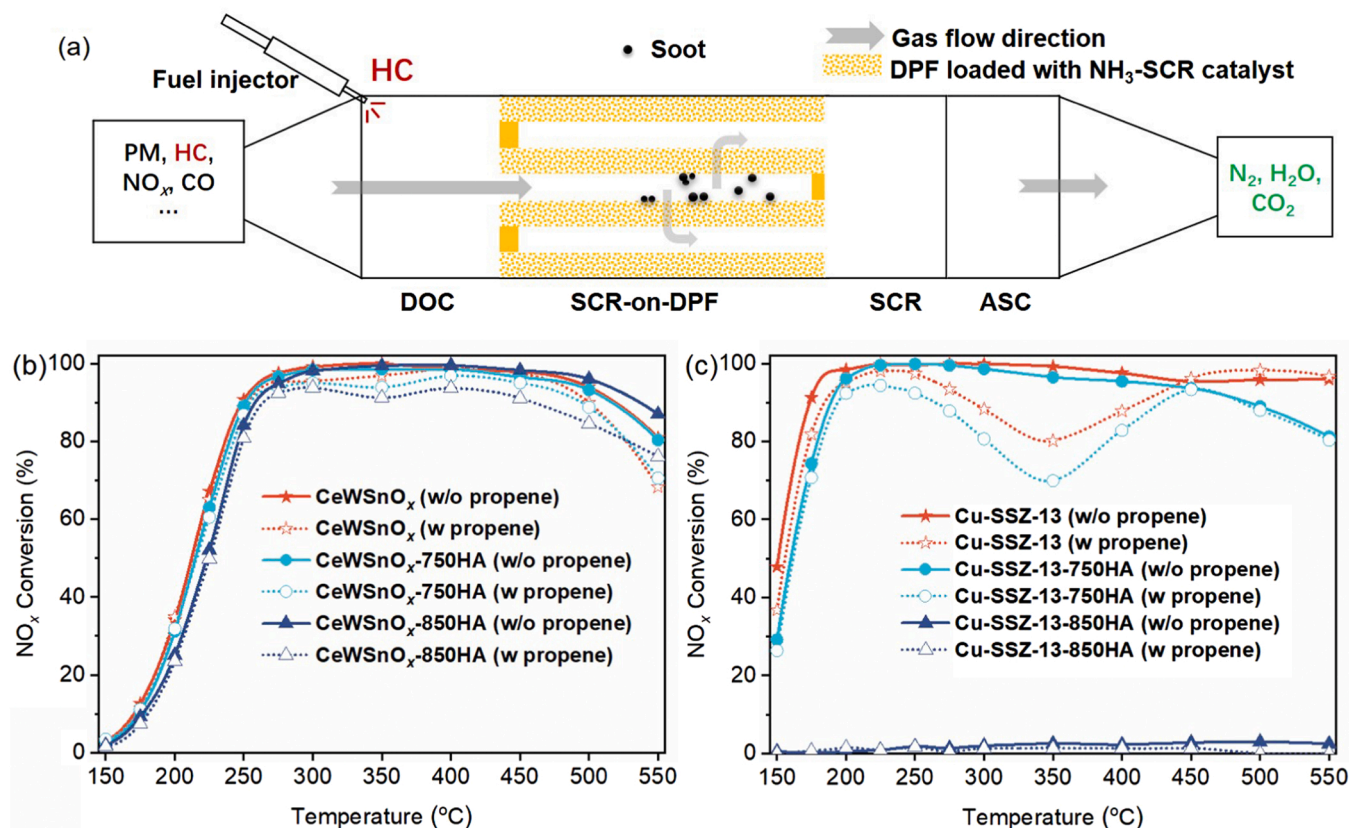


Fig. 2. Diesel after-treatment system with SCR-on-DPF configuration (a), effects of propene on the NH₃-SCR performance of hydrothermally aged CeWSnO_x (b) and Cu-SSZ-13 (c) catalysts. Reaction conditions: 530 ppm NH₃, 500 ppm NO, 859 ppm propene (when used), 5 vol% O₂, 5 vol% H₂O and balance N₂ with GHSV = 120, 000 h⁻¹.

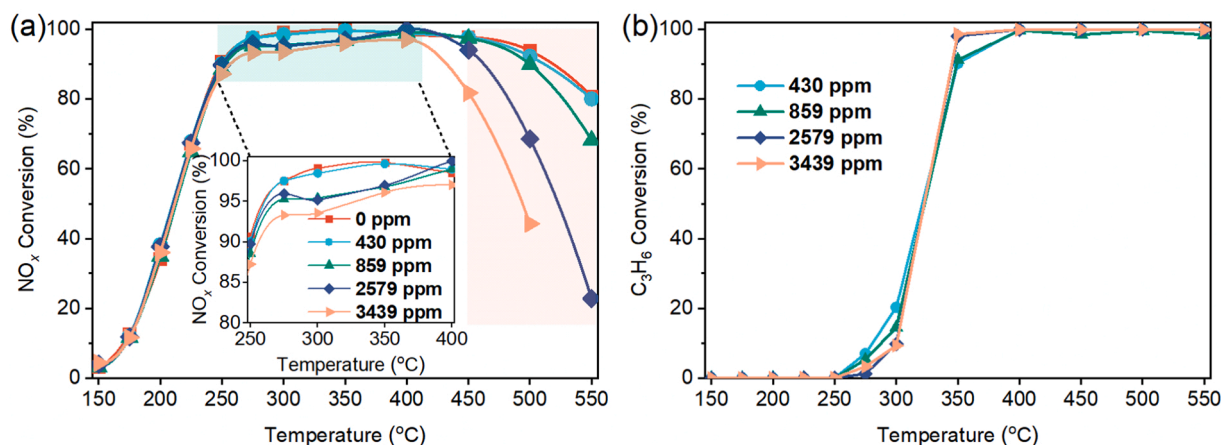


Fig. 3. Effects of propene concentration on the NO_x conversion (a) and propene conversion (b) of the CeWSnO_x catalyst for the NH₃-SCR reaction. Reaction conditions: 0–3439 ppm propene, 530 ppm NH₃, 500 ppm NO, 5 vol% O₂, 5 vol% H₂O and balance N₂ with GHSV = 120, 000 h⁻¹.

of 859 ppm propene was also investigated under different gas hourly space velocities (GHSVs). A loss in deNO_x efficiency was observed with increasing GHSV in the absence of propene (Fig. 4a), which should be ascribed to the lower residence time of reactant gas with the catalyst. Moreover, the addition of propene to the gas flow did not inhibit the NH₃-SCR performance of CeWSnO_x catalysts at low temperature (≤ 275 °C) under different GHSVs (Fig. 4a). At higher temperatures (> 275 °C), however, a significant decrease in NO_x conversion was observed when increasing the GHSV. In other words, the higher the GHSV was, the more significant the negative effects of propene on the NH₃-SCR performance became. Moreover, the propene conversion also

decreased with the increase in GHSV (Fig. 4b). In summary, the elevation of GHSV damaged the propene tolerance of the CeWSnO_x catalyst.

4. Discussion

4.1. Propene-related reactions that may occur on NH₃-SCR catalysts

When propene is present in the NH₃-SCR reaction flow, it may participate in the selective catalytic reduction of NO_x (propene-SCR, $C_3H_6 + (1.5x + 0.5) O_2 + 2 NO \rightarrow N_2 + 3 H_2O + 3 CO_x$ ($x = 1$ or 2)), coke formation, direct oxidation by O₂ (propene+O₂, $C_3H_6 +$

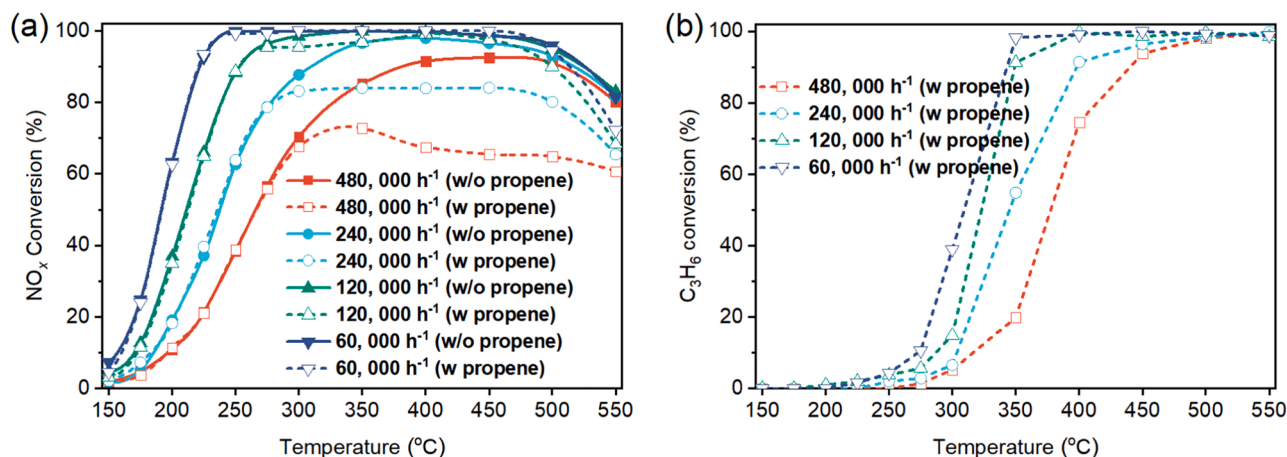


Fig. 4. Effects of gas hourly space velocity (GHSV) on the NO_x conversion (a) and propene conversion (b) of CeWSnO_x catalyst for the NH_3 -SCR reaction in the absence and presence of propene. Reaction conditions: 859 ppm of propene (when used), 530 ppm NH_3 , 500 ppm NO , 5 vol% O_2 , 5 vol% H_2O and balance N_2 with GHSV = 60, 000–480, 000 h^{-1} .

$(1.5x + 1.5) \text{O}_2 \rightarrow 3 \text{CO}_x + 3 \text{H}_2\text{O}$ ($x = 1$ or 2)) and ammoxidation of propene ($\text{propene} + \text{NH}_3 + \text{O}_2$).

The results of propene-SCR activity tests suggested that the maximum NO_x conversion of the CeWSnO_x catalyst in the propene-SCR reaction was only 11% (Fig. 5a), indicating that propene-SCR was not involved in the excellent anti-HC performance of the CeWSnO_x catalyst. For the propene-SCR reaction, the activation of propene and the formation of organic nitro species are critical [32]. To be specific, propene is first activated to enolic species and/or acetates on the catalyst surface, and subsequently these reaction intermediates combine with nitro species to form organic nitro species, which eventually decompose to N_2 , CO_2 and H_2O . The poor propene-SCR activity of CeWSnO_x can be explained by the fact that there is a large amount of active oxygen species present on the surface of this catalyst, according to a previous report [27], and the intermediates from propene activation are preferentially oxidized completely to CO_2 and CO on the metal oxide surface rather than being bound to the nitro species. Similarly, the $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst also showed poor propene-SCR performance (Fig. 5b). Instead, nearly 30% of NO_x was successfully reduced by propene on the Cu-SSZ-13 catalyst (Fig. 5c), which was in line with a previous study reporting that Cu-SSZ-13 could catalyze the propene-SCR reaction [23].

To investigate the deposition of coke over the catalysts, TG-MS analysis was performed on the hydrocarbon-poisoned (HCP) catalysts. As shown in Fig. 6a, significant weight loss can be observed in two stages for the Cu-SSZ-13-HCP, Cu-SSZ-13-750HA-HCP and Cu-SSZ-13-850HA-HCP catalysts. Specifically, the weight loss at 50–295 °C (Stage I) was due to the desorption of physically adsorbed H_2O , [33] and the weight loss at 295–650 °C (Stage II) was caused by the oxidation of coke by O_2 , according to the MS signal of CO_2 ($m/z = 44$) (Fig. 6b). The above results suggested that coke formation occurred on both the fresh and hydrothermally aged Cu-SSZ-13 zeolites in the presence of propene. Contrarily, only slight weight loss was observed in the TG-MS experiments for the different $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ and CeWSnO_x catalysts, suggesting that little carbonaceous deposit was formed on the surface of these two catalysts. To further investigate the side effects of cokes formed during hydrocarbon-poisoning treatment, we also tested the standard NH_3 -SCR performance of the different HCP catalysts, and the results (Fig. S6) suggested that the CeWSnO_x -HCP and $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ -HCP catalysts, on which no carbon deposits were observed, showed the same NH_3 -SCR performance as their fresh counterparts. For the Cu-SSZ-13-HCP catalyst, however, a marked decrease in the deNO_x efficiency at low temperature (≤ 250 °C) was observed. The above results make it clear that carbon deposits formed on the Cu-SSZ-13 catalyst

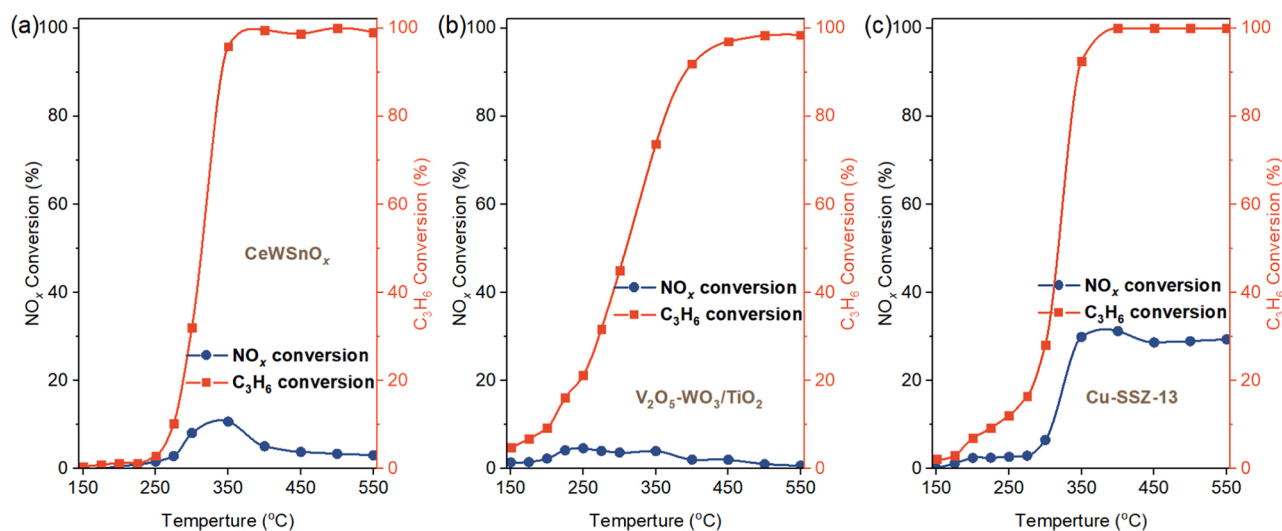


Fig. 5. Propene (right axis) and NO_x (left axis) conversion of the CeWSnO_x (a), $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ (b) and Cu-SSZ-13 (c) catalysts in the propene-SCR reaction. Reaction conditions: 859 ppm propene, 500 ppm NO , 5 vol% O_2 , 5 vol% H_2O and balance N_2 with GHSV = 120, 000 h^{-1} .

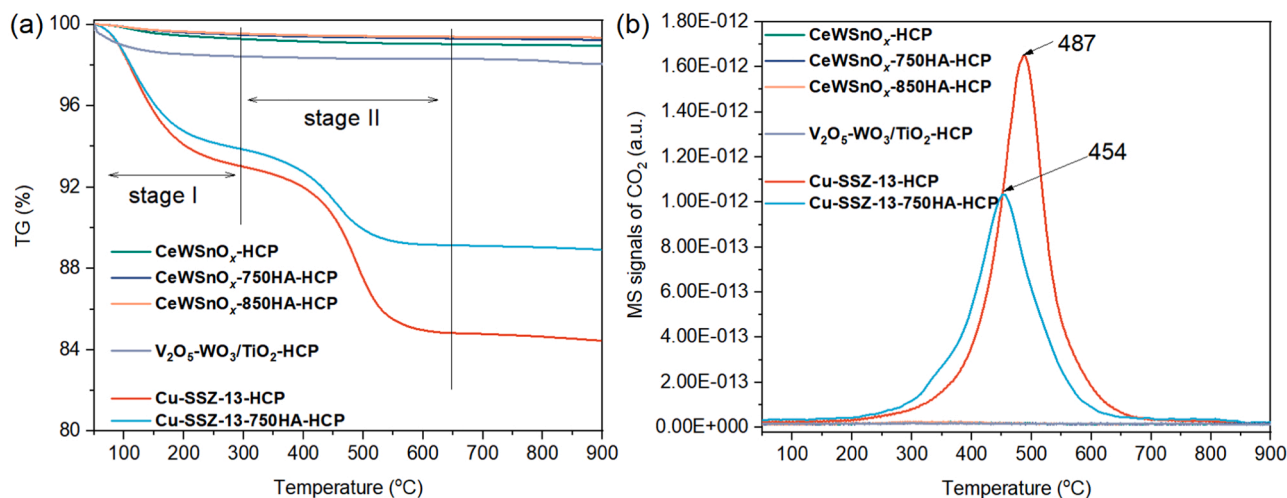
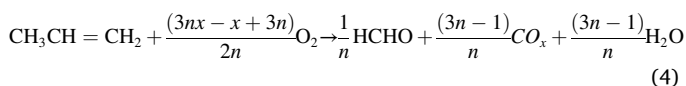


Fig. 6. TG (a) and MS (CO_2 , $m/z = 44$) (b) results of the different hydrocarbon-poisoned catalysts prepared by treating the fresh catalyst in an NH_3 -SCR atmosphere with 859 ppm propene at 350°C for 12 h.

during the hydrocarbon-poisoning treatment, thus covering the active sites and damaging the low-temperature NH_3 -SCR activity.

To further explore the reaction behavior of propene over the three NH_3 -SCR catalysts, the propene conversion (Fig. 7a–7c) and related product analysis results (Figs. 7d–7i) in the propene/ NH_3 and NO/O_2 (namely NH_3 -SCR in the presence of propene), propene/ NH_3 and O_2 and propene/ O_2 reactions were compared. Propene was converted to gaseous C-containing products including CO, CO_2 , HCN and HCHO during the propene/ NH_3 and NO/O_2 reaction (Fig. 7 and Fig. S7). There were two possible sources for the emission of HCN according to previous reports: HC-SCR and HC ammoxidation. The former case has been verified by many researchers. For example, Cant et al. pointed out that HCN can be a substantial product for the isobutane-SCR reaction over Fe-MFI catalysts [34–36]. Tamm et al. suggested that cyanide species ($-\text{CN}$) and the gas-phase species HCN were detected over $\text{Ag}/\text{Al}_2\text{O}_3$ catalysts for the propene-SCR reaction [37]. In this work, however, the HCN concentrations for the propene-SCR over the three catalysts (Fig. S8) were much lower than that for the propene/ NH_3 and NO/O_2 reaction (Fig. 7), thus excluding the possibility that the HCN gas was mainly derived from propene-SCR during the propene/ NH_3 and NO/O_2 reaction. Therefore, the gaseous HCN in the outlet gas should mainly originate from the HC ammoxidation reaction. This conclusion was further verified by the higher HCN concentration for the propene/ NH_3 and O_2 reaction than that for the propene/ NH_3 and NO/O_2 reaction over different catalysts (Figs. 7d–7f).

It should be emphasized that propene underwent incomplete oxidation over the three catalysts at medium temperatures, resulting in the formation of gaseous HCHO, according to the results of product analysis for the propene/ O_2 reaction (Figs. 7g–7i). Upon introducing NH_3 (namely in the propene/ NH_3 and O_2 reaction), however, HCHO disappeared and an equal amount of HCN was observed for the three catalysts. Recent studies suggested that HCHO could readily react with ammonia to form HCN [24,25,38,39]. For example, Ferri et al. suggested that formaldehyde from the gas phase likely reacts with pre-adsorbed NH_3 to form HCN [24,25]. Therefore, we speculated that propene present in the NH_3 -SCR flow first underwent a partial oxidation reaction to form gaseous HCHO via Reaction 4, and then HCHO reacted with NH_3 species to form HCN via Reaction 5 at medium temperatures:



($x = 1$ or 2 , and $n > 12$)



At higher temperatures, HCHO was not observed in the outlet for the propene/ O_2 reaction due to the occurrence of the total oxidation of propene. However, HCN was still observed in the outlet of propene/ NH_3 and O_2 and propene/ NH_3 and NO/O_2 reactions. Accordingly, we speculated that the HCN emission at high temperature should originate from the one-step reaction of propene with ammonia via the following reaction:



It should be noted that a seagull profile of C_3H_6 conversion was observed on the Cu-SSZ-13 catalyst for the propene/ NH_3 and O_2 reaction (Fig. 7c), and the presence of NH_3 actually promoted the conversion of C_3H_6 to CO and CO_2 at 300°C according to the C_3H_6 conversion and CO_x concentration profiles (Fig. S9). Considering the fact that NH_3 conversion in the propene/ NH_3 and O_2 reaction almost equals that in the NH_3 and O_2 reaction at 300°C over the Cu-SSZ-13 catalyst (Fig. S5), we excluded the possibility of the ammoxidation reaction of propene to HCN at 300°C since an increase rather than a drop in NH_3 conversion would be expected when NH_3 reacts not only with NO_x but also with C_3H_6 . We speculated that propene is oxidized on the catalyst surface at 300°C , and subsequently complexed with NH_3 to form organic intermediate species containing N such as HCONH_2 , HCOONH_4 and so on [38]. These species are less thermally stable and can further decompose to CO_x at low temperatures with the release of NH_3 . With the increase in temperature to 350°C , the ammoxidation reaction of propene to HCN was promoted according to the higher values of NH_3 conversion (Fig. S5) and HCN formation (Fig. S9), which would compete with the above decomposition reaction of nitrogen-containing organics for the same active sites, thus leading to the observed decrease in propene conversion at this temperature.

4.2. Comparison of propene ammoxidation reactions occurring over different catalysts

The CeWSnO_x catalyst showed lower HCN concentrations in the propene/ NH_3 and O_2 reaction and propene/ NH_3 and NO/O_2 reaction than those of the $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ and Cu-SSZ-13 catalysts (Figs. 7d–7f), indicating its relatively weak propene ammoxidation activity. In addition, the propene conversion levels of the CeWSnO_x catalyst in the propene/ NH_3 and NO/O_2 reaction were only slightly lower than that observed in the propene/ O_2 reaction (Fig. 7a). To sum up, the added propene in the NH_3 -SCR flow should be mainly oxidized by O_2 instead of

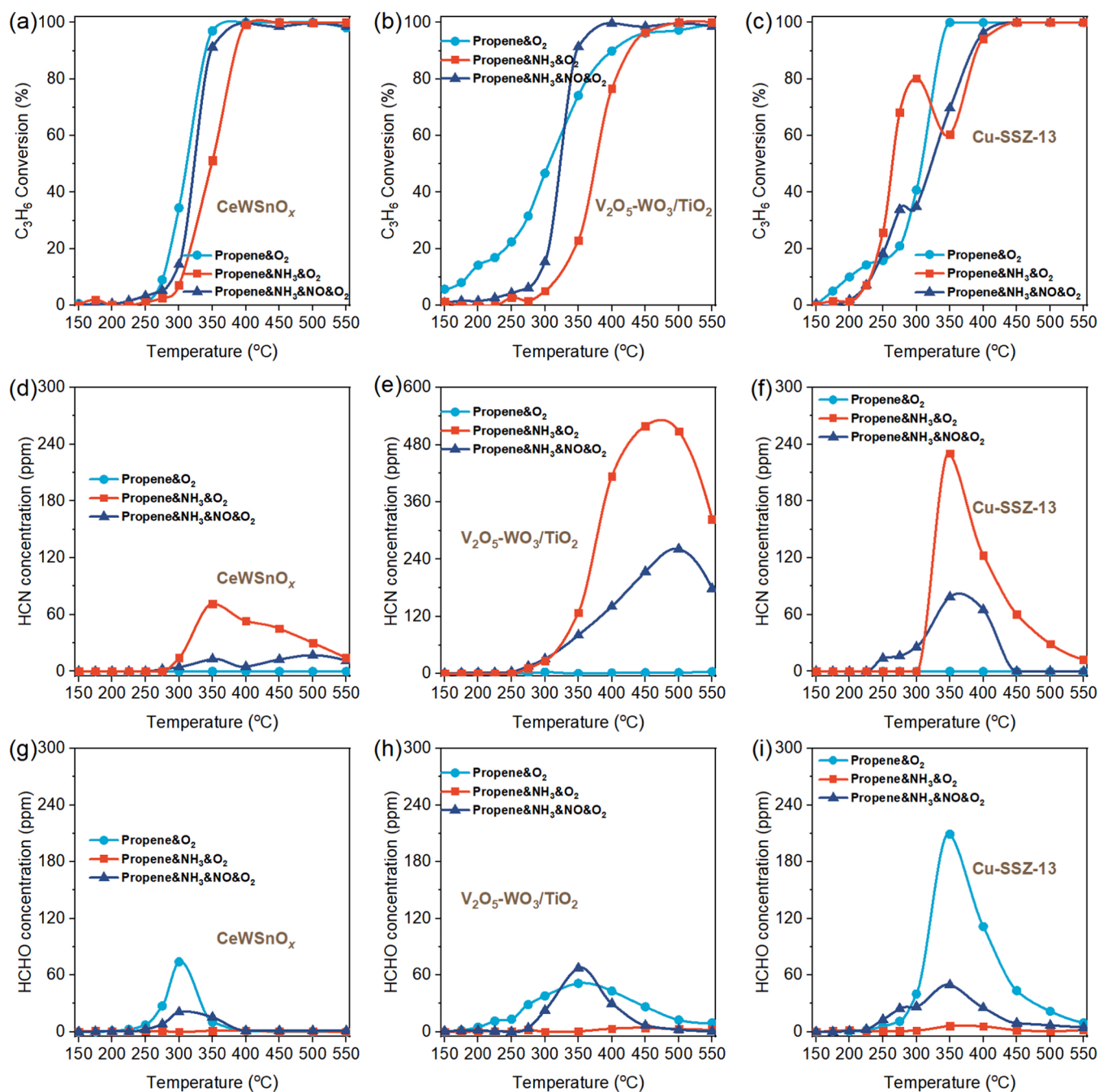


Fig. 7. Propene conversion, HCN concentration and HCHO concentration for the CeWSnO_x (a, d and g), $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ (b, e and h) and Cu-SSZ-13 (c, f and i) catalysts, respectively, in the propene & O_2 , propene & NH_3 & O_2 and propene & NH_3 & NO & O_2 reactions. Reaction conditions: 859 ppm propene, 530 ppm NH_3 (when used), 500 ppm NO (when used), 5 vol% O_2 , 5 vol% H_2O and balance N_2 with GHSV = 120, 000 h^{-1} .

participating in the propene ammoxidation reaction on the CeWSnO_x catalyst. According to our previous study, [27] Ce-W species served as the main active phase for the CeWSnO_x catalyst. We compared the HC resistance of CeWO_x and CeWSnO_x catalysts to confirm the role of individual components of the CeWSnO_x catalyst in HC tolerance. The corresponding results (Fig. S10-S13) suggested that CeWO_x showed poor HC tolerance due to the occurrence of the ammoxidation reaction of propene to HCN, and that SnO_2 played an important role in avoiding this side reaction via promoting the redox capacity of this catalyst. For the $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst, the highest HCN emissions were produced in both the propene & NH_3 & NO & O_2 and propene & NH_3 & O_2 reactions (Fig. 7e), which was in line with having the lowest HC tolerance among the three catalysts (Fig. 1a). As for the Cu-SSZ-13 catalyst, the formation

of HCN (Fig. 7f) and the loss of NH_3 -SCR performance (Fig. 1a) occurred simultaneously at 350–450 °C in the presence of propene. The results above suggested that the propene ammoxidation reaction occurred on the Cu-SSZ-13 and $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts when propene was present in the NH_3 -SCR gas flow, thus competing with the NH_3 -SCR reaction for NH_3 species and resulting in a decrease in NO_x reduction.

A recent study by Shuai et al [14] showed that the highest NO_x conversion efficiency of cc-SCR and main SCR for heavy-duty diesel occurs at 350 °C. Based on these results, NH_3 -SCR tests with/without propene were performed at 350 °C to further investigate the side effects of the propene ammoxidation reaction. When propene was absent from the feed gas, the CeWSnO_x , $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ and Cu-SSZ-13 catalysts showed ~100% NO_x conversion (Fig. 8a, 8c and 8e). Upon injecting

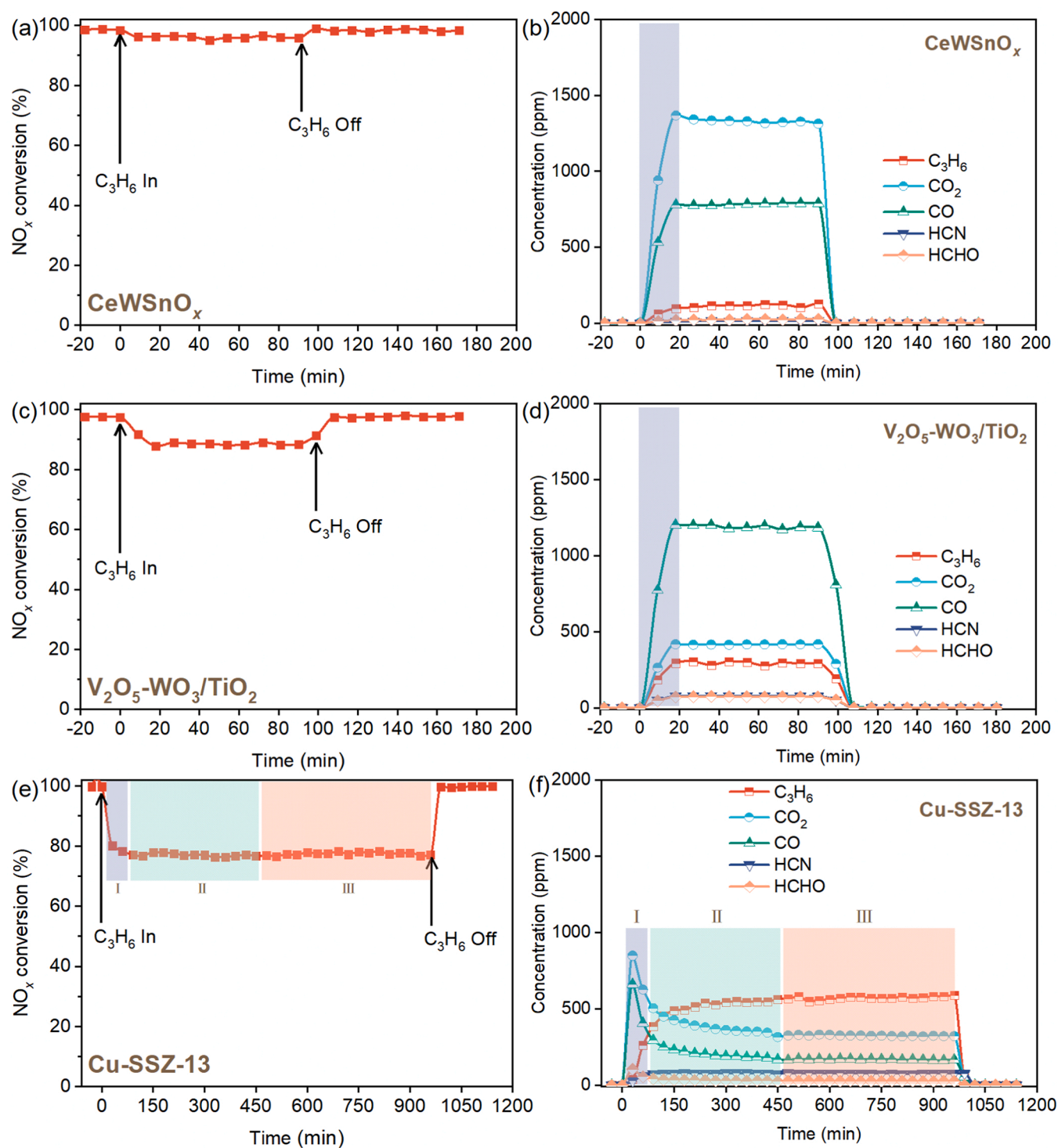


Fig. 8. NO_x conversion (left) and (right) gaseous C-containing product concentration during transient propene poisoning under standard conditions over CeWSnO_x (a-b), V₂O₅-WO₃/TiO₂ (c-d) and Cu-SSZ-13 (e-f) catalysts. Reaction conditions: 530 ppm NH₃, 500 ppm NO, 859 ppm propene (when used), 5 vol% O₂, 5 vol% H₂O and balance N₂ with GHSV = 120, 000 h⁻¹, T = 350 °C.

propene, NO_x conversion decreased respectively from 98% to 96% and from 97% to 88% for the CeWSnO_x and V₂O₅-WO₃/TiO₂ catalysts (Figs. 8a and 8c), which was accompanied by the generation of HCN, HCHO and a large amount of CO_x (x = 1 and 2). Specifically, steady state was reached within 20 min with the formation of ~18 ppm of HCN for CeWSnO_x (Fig. 8b) and ~77 ppm of HCN for V₂O₅-WO₃/TiO₂ (Fig. 8d), respectively. For the Cu-SSZ-13 catalyst, the NO_x conversion dropped to 77% after 60 min of propene introduction, and then

remained unchanged (Fig. 8e). Moreover, HCN, HCHO and CO_x were detected over time in the outlet gas over this catalyst (Fig. 8f). Interestingly, the concentration of CO_x reached a peak value at t = 30 min and then slowly decreased until t = 450 min. It could be inferred that the gradually accumulated coke deposits covered the active sites of the Cu-SSZ-13 catalysts, thus resulting in a decrease in the concentration of CO_x produced by propene oxidation or the propene-SCR reaction. After switching off propene, full SCR activity was regained immediately for all

three catalysts (Figs. 8a, 8c and 8e), further confirming that the deactivation caused by the dosing of propene at 350 °C for the three catalysts was mainly due to HCN formation instead of coking deposition, since coke can be removed only when the temperature is above 350 °C (Fig. 6). It should be noted that an ammoxidation side reaction also occurred over the V_2O_5 - WO_3 /TiO₂ catalyst in the presence of toluene or *n*-pentane since the HCN concentration (Fig. S14) correlated well with the decrease in SCR activity over this catalyst (Figs. 1b and 1c).

Although the CeWSnO_x catalyst showed excellent HC tolerance, some strategies including hydrothermal aging treatment (Fig. 2a), increasing the propene concentration (Fig. 3a) or increasing the GHSV (Fig. 4a) could all result in a decrease in the NO_x conversion of the CeWSnO_x catalyst for the NH₃-SCR reaction in the presence of propene to varying degrees. Meanwhile, an increase of the HCN concentration in the corresponding outlet gas was detected (Fig. 9). In particular, increasing the GHSV had the most significant inhibitory effects on the NH₃-SCR catalytic activity of the CeWSnO_x catalyst in the presence of propene. According to a previous report,[39] complete conversion of HCs is hard to achieve at high GHSVs due to the low diffusion rate of HCs from the gas phase to the catalyst surface. To validate this claim, we investigated the effects of GHSV on the C₃H₆ conversion and product compositions of the CeWSnO_x catalyst for the propene&NH₃&O₂ reaction. The results suggested that the increase in GHSV did inhibit the formation of CO₂ (Fig. S15a-S15b) and promoted the formation of CO and HCN (Fig. S15c-S15d). Since the increase in GHSV was realized by reducing the mass of the catalyst used while keeping the composition of the feed gas unchanged, the number of reactant molecules being provided to per unit active site increased with the increase in GHSV. As a result, the competition for active sites among NH₃-SCR, propene ammoxidation and complete propene oxidation reactions became more intense. Based on a previous report[40], propene ammoxidation is a partial oxidation reaction. The high GHSV, therefore, resulted in inhibition of complete propene oxidation to CO₂ (Fig. S15) and the promotion of propene ammoxidation to HCN (Fig. 9c). Similarly, hydrothermal aging treatment caused a decrease in the redox ability of the CeWSnO_x catalyst,[27] thus also intensifying the ammoxidation of propene to a certain extent (Fig. 9a). Moreover, increasing the propene concentration caused Reaction (4–6) to proceed in the forward direction, which was consistent with the increase in the HCN concentration (Fig. 9b) and the decrease in NO_x conversion (Fig. 3a). The above

results further suggested that the occurrence of the propene ammoxidation reaction could result in the loss of deNO_x efficiency for the CeWSnO_x catalyst in the presence of propene under some conditions.

4.3. The inhibition of HCN generation

During the NH₃-SCR reaction with C₃H₆, incomplete oxidation of hydrocarbons can easily trigger the propene ammoxidation reaction, which generates gaseous HCN. Based on this work, the generation of HCN can be reduced by two routes: 1) HCN formation could be inhibited to some extent via adjusting the reaction conditions. For the CeWSnO_x catalyst, the partial oxidation was suppressed under low GHSVs, and thus the side reactions of HC ammoxidation to HCN can be effectively prevented. 2) Modification of the NH₃-SCR catalyst by adding a strongly oxidizing component could effectively reduce the generation of HCN. Actually, the addition of oxidizing components to enhance the hydrocarbon resistance of catalysts has been tried by several researchers. For example, Martinovic et. al significantly improved the HC resistance of Cu-SSZ-13 by mixing CeO₂-SnO₂ and Cu-SSZ-13 to form a composite catalyst [12]. Zhao et. al prepared a series of hybrid catalysts with enhanced C₃H₆ resistance by mechanical mixing of Fe-Beta and MnO_x/CeO₂ [41]. They all pointed out that the weakening of competitive adsorption between C₃H₆ and NO_x due to the addition of oxidizing components is the main reason for the improvement of the C₃H₆ resistance of catalysts. In this work, we suggest that the introduction of SnO₂ to CeWO_x greatly improved the propene resistance of CeWO_x by inhibiting the propene ammoxidation reaction, which was different from the previous studies.

4.4. DRIFTS analysis

Based on the above results, the propene ammoxidation reaction to give HCN as a product proceeded strongly over the V_2O_5 - WO_3 /TiO₂ and Cu-SSZ-13 catalysts when propene was present in the NH₃-SCR atmosphere, thus resulting in the loss of NH₃-SCR performance due to the lack of NH₃. For the CeWSnO_x catalyst, surprisingly, weaker propene ammoxidation was observed. To reveal the underlying reasons for this discrepancy, in-situ DRIFTS experiments were performed over the CeWSnO_x catalyst.

According to the in-situ DRIFTS results of propene+O₂ co-adsorption

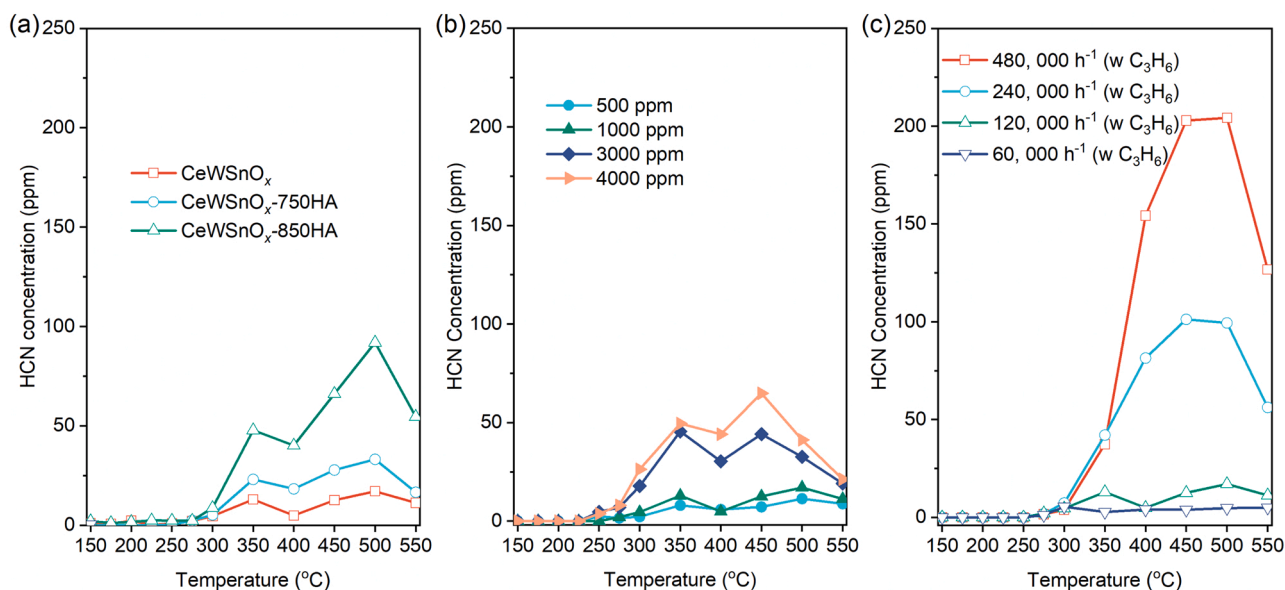


Fig. 9. Effects of hydrothermal-aging treatment, propene concentration and GHSVs on HCN formation for the NH₃-SCR reaction in the presence of propene over the CeWSnO_x catalyst. Reaction conditions can be found in Fig. 2, Fig. 3 and Fig. 4, respectively.

experiments at 200–500 °C, different hydrocarbon oxygenates from the partial oxidation of propene were observed on the surface of the CeWSnO_x catalyst (Fig. 10a). Specifically, the bands at 1573 cm⁻¹ could be assigned to the $\nu_{as}(\text{COO}^-)$ of carboxylates that formed due to the straightforward catalytic oxidation of propene [41–43]. The slightly weaker bands at 1414–1379 cm⁻¹ were related to the $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-) + \delta(\text{CH})$ vibrations of formate species [38]. The band at 1658 cm⁻¹ could be assigned to the $\nu_{C=O}$ vibration of acrolein (CH₂=CH-CHO), acetone (CH₃COCH₃) or acrylate species [37,42]. The intensity of IR bands first increased and then decreased with increasing temperature, reaching a maximum at 300 °C over the CeWSnO_x catalyst. The highest concentration of gaseous HCHO for the propene+O₂ reaction was also observed at 300 °C (Fig. 7g). These results proved that the partial oxidation reaction of propene took place most strongly at 300 °C. At higher temperatures above 300 °C, the IR bands of weakly adsorbed CO₂ (2375 and 2309 cm⁻¹) [44] were observed, indicating that the deep oxidation of hydrocarbon oxygenates to CO_x, which was thermodynamically favorable, occurred on the CeWSnO_x catalyst. Accordingly, the interaction among propene, NH₃ and O₂ was further investigated at 300 °C by performing the in-situ DRIFTS of NH₃ + O₂ and propene+NH₃ + O₂ co-adsorption experiments. After exposing the catalyst to a flow of NH₃ + O₂, the bands from NH₄⁺ on the Brønsted acid sites (1434 cm⁻¹) and coordinated NH₃ on Lewis acid sites (1170, 1232, 1266 and 1607 cm⁻¹) were observed on the surface of the CeWSnO_x catalyst (Fig. 10b). When simultaneously passing propene+NH₃ + O₂ over the CeWSnO_x surface, the IR vibrations of the partial oxidation products of propene as well as NH₃/NH₄⁺ adsorbed species were observed (Fig. 10c). As a result, the presence of propene in the feed gas had little effect on the NH₃ adsorption performance. It is worth noting that no key intermediates [37,38,45] to generate HCN, including adsorbed -NCO (2232 cm⁻¹) and -CN (2130 and 2160 cm⁻¹), or HCONH₂ (1685, 1602, and 1394 cm⁻¹), were observed on the surface. These results could be explained by the fact that although the propene+O₂ reaction to generate HCHO occurs strongly at 300 °C, the CeWSnO_x catalyst cannot further catalyze the HCHO+NH₃+O₂ reaction to form HCN via Reaction 5 at this temperature. As a result, the presence of propene showed little effect on the NH₃-SCR performance of this catalyst at 300 °C. At higher temperatures above 300 °C, propene was directly oxidized to CO_x instead of HCHO due to the strong oxidation capacity, which could be verified by the higher concentration of CO₂ in the outlet than that of the V₂O₅-WO₃/TiO₂ and Cu-SSZ-13 catalysts at 350 °C (Fig. 8), thereby avoiding the consumption of ammonia gas.

5. Conclusion

The tolerance of CeWSnO_x, V₂O₅-WO₃/TiO₂ and Cu-SSZ-13 catalysts towards propene, toluene and *n*-pentane was comparatively studied in this work. Specifically, all three HCs showed inhibiting effects on the NH₃-SCR activity of the V₂O₅-WO₃/TiO₂ catalyst due to the occurrence of an ammoxidation reaction that competed with the NH₃-SCR reaction for NH₃ species and resulted in the emission of a significant amount of highly toxic HCN. For the Cu-SSZ-13 catalyst, serious loss of deNO_x efficiency occurred at medium temperatures in the presence of propene. The reaction path involved propene undergoing partial oxidation reaction on the Cu-SSZ-13 catalyst to form HCHO, whereupon HCHO continued to react with ammonia to form HCN. Meanwhile, coke deposition also occurred on the Cu-SSZ-13 catalyst after propene-poisoning treatment at 350 °C, which covered the active copper species on the Cu-SSZ-13 catalyst and damaged the NH₃-SCR activity at 150–250 °C. For the CeWSnO_x catalyst, however, the deNO_x activity of fresh and hydrothermally aged catalysts at 750 °C was not significantly suppressed after adding ≤ 859 ppm propene into the feed gas stream with GHSV ≤ 120, 000 h⁻¹. Such superior propene poisoning tolerance was tightly correlated with the strong capacity for propene oxidation to CO₂, excellent anti-coking ability and weak propene ammoxidation activity of the CeWSnO_x catalyst. Even after hydrothermal-aging treatment at 850 °C for 16 h, the CeWSnO_x catalysts still removed > 80% NO_x at 250–500 °C in the presence of propene. The anti-hydrocarbon-poisoning ability and NH₃-SCR performance gives CeWSnO_x great potential for application in advanced after-treatment systems such as those with LNT-SCR, SCR-on-DPF or cc-SCR configuration.

CRediT authorship contribution statement

Jingjing Liu: Data curation, Writing – original draft, Investigation, Software. **Xiaoyan Shi:** Writing – review & editing, Data curation, Funding acquisition. **Yunbo Yu:** Writing – review & editing, Funding acquisition. **Mengyuan Zhang:** Investigation, Data curation. **Diru Liu:** Investigation, Data curation. **Hong He:** Conceptualization, Funding acquisition, Project administration, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

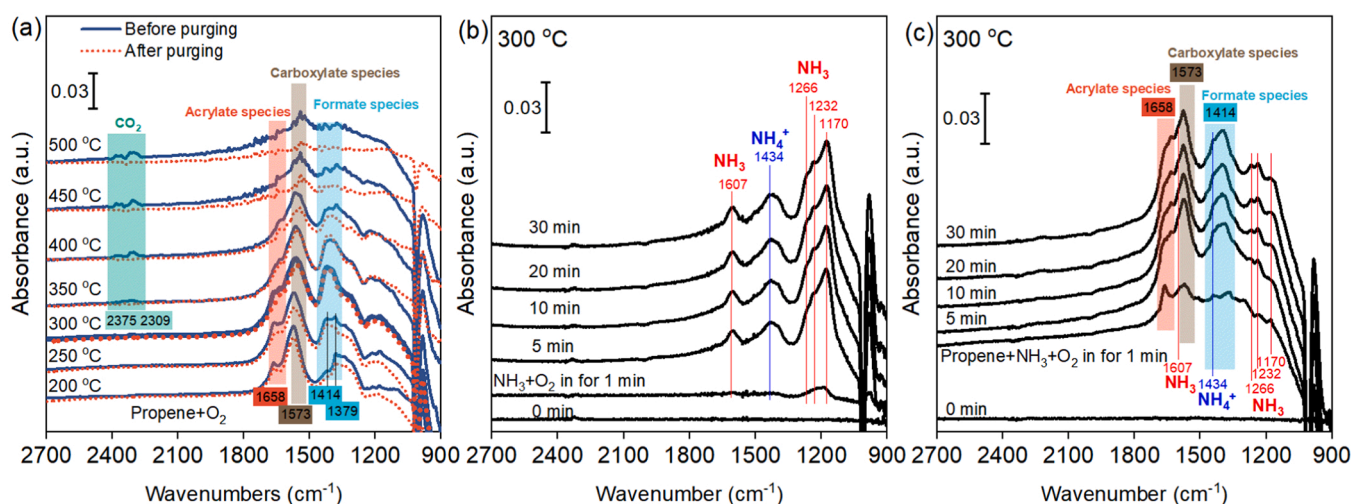


Fig. 10. In-situ DRIFTS results obtained by passing a flow of propene+O₂ at 200–500 °C (a), NH₃ + O₂ at 300 °C (b) and propene+NH₃ + O₂ at 300 °C (c), respectively, over the CeWSnO_x catalyst. Reaction conditions: 530 ppm NH₃ (when used), 859 ppm propene (when used), 5 vol% O₂ and balance N₂.

Data availability

Data will be made available on request.

Acknowledgment

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2022.122283](https://doi.org/10.1016/j.apcatb.2022.122283).

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